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PATENT SPECIFICATION

(11) 1 426 423

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- (21) Application No. 52417/74 (22) Filed 4 Dec. 1974
 (44) Complete Specification published 25 Feb. 1976
 (51) INT CL² C25D 11/10, 11/14, 13/20
 (52) Index at acceptance C7B 10B 13 15X 16A 2F
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(54) METHOD OF PRODUCING COLORED ANODIC COATING ON ALUMINUM AND ITS ALLOYS

(71) We, FUJISASH INDUSTRIES, LTD., a Company organized and existing under the laws of Japan, of 135, Nakamaruko, Nakahara-ku, Kawasaki-shi, Kanagawa-ken, Japan, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a method of producing a colored anodic coating on aluminum and its alloys by passing a direct current through an aqueous electrolyte solution.

The colored anodic coating on aluminum or its alloys is accomplished by immersing an anode consisting of the aluminum or its alloys, and at least one cathode consisting of stainless steel or other metallic materials into the electrolyte solution and passing direct current between the anode and the cathode. Electrolyte solutions which produce colored coatings and which are already known in the art comprise: sulphophthalic acid and sulfuric acid; phenol sulfonic acid and sulfuric acid; and, sulfosalicylic acid and at least one of sulfuric acid, lactic acid, maleic acid, cresylic sulfonic acid and oxalic acid.

The colors of coatings produced by the conventional electrolytes are rather dull and are not transparent. Said coatings produced by the conventional electrolytes can be stably colored only if an oxide film on the aluminum or its alloy becomes thick, for example 10 microns or more.

The conventional colored coatings may be covered by inorganic or organic paint film, such as thermosetting resin film, when it is desired to use the coated article in a corrosive atmosphere, as the coating by anodic oxidation does not have sufficient weather resistant properties. The conventional colored coatings, however, are not suitable for such applications, because it is difficult to heat aluminum to the drying temperature needed to cure paint coated on the thick oxide film. For example, in a case where thermosetting resin film is em-

ployed and is cured at a high temperature, for example 150°C, the colored oxide coatings tend to develop fissures with the result that the coated article is unacceptable for practical application. The film of paint formed on the oxide coating is, therefore, usually cured at such a low temperature that the film of paint does not have the desired properties.

In accordance with the present invention, there is provided a method of producing colored anodic coating on aluminum and its alloys comprising: providing at least one cathode; immersing the aluminum or its alloy as an anode into an aqueous electrolyte comprising aromatic sulfonic acid; passing a direct current through the electrolyte solution between the anode and the cathode to obtain a colored anodic coating on the aluminum or its alloy; wherein an improvement comprises employing, as said aqueous electrolyte, an aqueous electrolyte solution containing (a) aromatic sulfonic acid and (b) at least one member selected from formic acid and formate salts.

The combination of aromatic sulfonic acid and formic acid or formate to produce colored coatings has not been known prior to the present invention, because an electrolyte containing either aromatic sulfonic acid or formic acid was not recognized as being capable of forming desired coatings on aluminum and its alloys. An electrolyte solution containing only sulfosalicylic acid as the aromatic sulfonic acid has been recognized to bring about electric discharge accompanied by sparks on the surface of aluminum or its alloys. The aluminum treated in this electrolyte solution is exposed to pitting corrosion during the electrolytic coating. This electrolyte solution further does not provide the favorable conditions needed in order to increase the thickness of the oxide film being formed, on the aluminum or its alloys, to a sufficient value. It is also known that an electrolyte solution containing formic acid exclusively, causes the formation of pitting on the aluminum surface and does not provide sufficiently thick coatings even if the electric current density and the

voltage are widely changed. In order to form the anodic coating on aluminum using an electrolyte solution containing formic acid exclusively, it is required that the temperature of the electrolyte be raised so as to be close to its boiling point and the formic acid contained in the electrolyte must be in an extremely high concentration. Since monocarboxylic acids, in which the formic acid is included, belong to the monobasic acid category, said monocarboxylic acids dissociate hydrogen in an amount considerably lower than that required to initiate the anode reaction. Accordingly, monocarboxylic acid having low dissociation constants must be present in an extremely high concentration and must be heated also to its boiling point. In addition to these disadvantages, monocarboxylic acids bring about pitting corrosion on the aluminum anode and the destruction of the oxide film, when said monocarboxylic acids are present in the electrolyte solution in a moderate or low concentration. In addition to the low dissociation constants of the monobasic acids, the adsorption of these acids on the aluminum anode is not suitable for forming oxide film on the aluminum compared to the adsorption of polybasic acids. Namely, the monobasic acids dissociating the hydrogen are adsorbed and placed on the aluminum anode in a smaller force than the polybasic acids, thereby failing to homogeneously and actively oxidize the aluminum surface.

Attempts were made to remove one of the disadvantages of monobasic acids, i.e. the inactive adsorption phenomenon of anions dissociated from formic acid, by incorporating another ingredient into the electrolyte solution. According to one of the attempts, an electrolyte solution containing oxalic acid in addition to the formic acid was proposed. This proposed electrolyte solution, however, did not make it possible to produce both vivid, transparent colored coatings and thin coatings. Colored coatings are obtained using the proposed electrolyte solution only when the electrolysis time is extended until the coatings grow to a thickness of approximately 40 microns. According to another attempt, sulfuric acid was added into the electrolyte consisting of formic acid so as to provide an electrolyte with improved electrical conductivity. This attempt, however, also did not prove to be successful, since aluminum treated in this electrolyte solution was still subject to the pitting corrosion.

The present inventors found that aromatic sulfonic acid enables the disadvantages of the formic acid to be overcome. Formic acid in the presence of aromatic sulfonic acid is free from the harmful corrosion effect, thereby ensuring that a stable oxide film can be favorably formed.

As far as the inventors understand the mechanism of coloration, the aromatic sulfonic

acid incorporated in the electrolyte solution is decomposed during electrolysis, following which a part of the substances decomposed from the aromatic sulfonic acid remains in the film being formed, allowing vivid colors to be developed on the aluminum.

The colors of the oxide film produced by the above process according to the present invention have various hues depending upon, first of all, the thickness of the film and, secondly, on the kinds of material treated. The colors are marked by a high degree of saturation and transparency irrespective of the thickness and the kinds of materials treated.

The throwing power of the electrolyte solution can be increased to twice the throwing power of the conventional electrolyte solution. Therefore, when the aluminum or its alloy shapes are piled in a supporting cage and then dipped in the electrolyte solution, a gap provided between each shape is decreased to half the size of the gap defined between each shape in order to form desired coatings on the shapes according to the conventional electrolyte.

The inventors have also found that formate salts including nickel formate and ammonium formate can be used, with or without formic acid, as the above-described second member of the electrolyte solution so as to achieve the advantageous results mentioned above. Therefore, at least one of formic acid, nickel formate and ammonium formate should be preferably used as one of the essential components of the electrolyte solution.

Further, the aromatic sulfonic acid should preferably be selected from sulfophthalic acid and sulfosalicylic acid.

According to an embodiment of the invention, the electrolyte contains an aromatic sulfonic acid in an amount of from 10 to 500 g/litre and at least one member selected from the group consisting of formic acid and formate salts in an amount of 5 to 200 g, in terms of the weight of the formic acid, per litre of the electrolyte. The electrolyte solution described may be employed over the following range of operating conditions: 0.5 to 5 ampere/square decimeter of aluminum (alloy) surface of current density: 20 to 120 volts of voltage applied between the anode and the cathode; 1 to 150 minutes of electrolysis time.

The electrolyte should preferably contain from 10 to 40 g/litre of at least one member of the formic acid and formate group. When it is desired to produce a satin finished surface, the content of at least one member from the formic acid and formate group should be in excess of 40 g/litre. In this case, surface defects and seams formed by dies on the basic metal disappear. On the other hand, when lustrous oxide coatings are desired, the content of at least one member from the formic acid or formate group should not exceed 10 g/litre.

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The coatings of various hues are produced by adjusting the operation conditions, i.e. the current density, voltage and time period of treatment, so that the thickness of the film is changed within a wide range.

5 According to another embodiment of the invention, the electrolyte solution containing components within the particular ranges already described, is employed over the following operating conditions: 1 to 3
10 amperes/square decimeter of aluminum (alloy) surface of current density; 25 to 80 volts of voltage, and; 5 to 20 minutes of an electrolysis time. In this embodiment, the colored, extremely thin, i.e. from 2 to 20 microns, coatings can be produced. A coating of 2 microns
15 in thickness can be produced by selecting operating conditions substantially equal to the lower limits of said operating conditions. The thickness of the coatings does not exceed 20
20 microns when the coating process is carried out at operating conditions substantially equal to the upper limits. This method, which is capable of forming a thinly coated film, provides some advantages. First of all, the time of
25 the electrolytic coating can be shortened by as much as a fourth to a half as compared to the conventional process. Secondly, the thermosetting resin paint coated on the aluminum can be cured at a high temperature, for
30 example 180°C, without danger of generating fissures in the oxide film. In addition, the paint coating is firmly adhered to the surface of the aluminum or its alloys. Thirdly, the qualities
35 of the thinly coated oxide film, such as wear resistance, adhesion and corrosion resistance, are not inferior compared to those of conventional thickly coated film. Fourthly, since the
40 oxide film exhibiting minute pores with a diameter ranging from 100 to 1000 angstroms can be colored when the film reaches a very small thickness, paint can be infiltrated into
45 the pores using an electrodeposit painting method, thereby enabling said electrodeposit coating to be applied on the anodic coated article. Even if a part of the paint, which is
50 deposited on the aluminum (alloy) surface, exfoliates therefrom, the remaining part of the paint, which is infiltrated into the pores, helps to resist corrosion. The resistance against the alkali solution of the aluminum, or its alloy, which is subjected to the colored anodic coating and then to the painting, is, therefore,

superior to the aluminum (alloy) produced by the conventional method.

55 According to a further preferable embodiment of the invention, the electrolyte for colored coating of aluminum or its alloys contains (a) aromatic sulfonic acid, (b) at least
60 one member selected from formic acid and formate salts, and (c) at least one member selected from sulfuric acid and water soluble sulfate or bisulfate salts. The water soluble
65 sulfates and ammonium sulfate. The water soluble bisulfates salts include, for example, metal bisulfates and ammonium sulfates. The aforementioned member (c) enables the electrical
70 conductivity of the electrolyte to be adjusted in a such manner that the electrolyte operation can be carried out at a lower voltage. The member (c) further promotes the formation of
said oxide film and the coloration thereof.

According to still another preferable embodiment the electrolyte contains (a) aromatic sulfonic acid in an amount of from 10 to 500
75 g/litre, (b) at least one member selected from formic acid and formate salts in an amount of from 5 to 200 g, in terms of the weight of formic acid, per litre of the electrolyte and
80 (c) at least one member selected from sulfuric acid and water soluble sulfate or bisulfate salts in an amount not higher than 5 g, in terms of the weight of the sulphuric acid, per
85 litre of the electrolyte, more preferably 0.5 to 2 g/litre, and the direct current is passed at a current density of from 0.5 to 5 ampere/square decimeter of aluminum (alloy) surface over
90 a period of 1 to 150 minutes, and a voltage of from 20 to 100 volts is applied between the anode and the cathode.

According to a yet another preferable embodiment of the invention, the electrolyte solution containing said three components within the particular ranges according to the
95 foregoing still another preferable embodiment is employed under the following operating conditions: 5 to 20 minutes; 1 to 3 amperes/square decimeter of current density; 25 to 80
volts of voltage, so that the colored coatings
100 have a thickness of from 2 to 20 microns.

The invention will be illustrated by way of the following examples. The aluminum or its alloy used in these Examples had the following compositions.

TABLE I

Designation (Form)	Cu	Si	Fe	Mn	Mg	Zn	Cr	Ti	Al
A1100 (sheet)	0.14	0.11	0.56	0.01	0.00	0.02	0.01	0.01	rest
A3003 (sheet)	0.20	0.60	0.70	1.0-1.5	-	0.10	-	-	rest
A6063T ₆ (snape)	- 0.10	- 0.2-0.6	- 0.35	- 0.10	- 0.45-0.90	- 0.10	- 0.10	- 0.10	- rest

obtained colored oxide films were as hard as the conventional films and exhibited excellent weather resistance.

Example 1.

Aluminum sheets and aluminum alloy shapes were degreased and etched prior to the anodic coating. The aluminum sheets and aluminum alloy shapes were immersed in a solution as an anode and a stainless steel bars were immersed in the solution as cathodes. The conditions of treatment and the results are shown in Table II.

In this table, the primed numbers indicate that the treatments were carried out under the same conditions as those of the basic numbers except for the length of treatment times. The

Example 2.

The aluminum alloy shapes treated according to conditions No. 6 of Example 1 were subjected to electrophoretic painting. The painted shapes were heated at 180°C for 30 minutes without formation of cracks in the colored oxide film and without discoloration of this film.

TABLE II

No.	Aluminum Designation	Aromatic Sulfonic Acid. g/l	Formic Acid or Formate. g/l	Sulfuric Acid or Sulfate. g/l	Current Density A/dm ²	Voltage. Volts	Temperature °C	Time. minutes	Thickness. microns	Color
1	A1100	Sulfosalicylic acid. 65g/l	Formic Acid. 15g/l	—	2.0	45-100	20	15	8	Yellowish umber
2	A1100	Sulfosalicylic acid. 50g/l	Formic Acid. 12g/l	Sulfuric acid 0.8g/l	3.0	45-60	20	12	8	Yellowish umber
2'	do	do	do	do	do	do	do	24	17	Umbre
3	A3003	Sulfosalicylic acid. 65g/l	Formic acid. 15g/l	Sulfuric acid 1g/l	1.0	50-70	20	12	3	Gray
3'	do	do	do	do	do	do	do	30	7	Dark gray
4	A6063T ₅	Sulfosalicylic acid. 70g/l	Formic acid. 18g/l	Sulfuric acid 1.2g/l	1.5	45-55	20	12	4	Light umber
4'	do	do	do	do	do	do	do	24	8	Yellowish brown
5	A6063T ₅	Sulfosalicylic acid. 70g/l	Formic acid. 18g/l	Sulfuric acid 1.2g/l	3.0	45-60	20	12	9	Yellowish brown
6	A6063T ₅	Sulfosalicylic acid. 70g/l	Formic acid. 18g/l	Sulfuric acid 1.2g/l	3.0	45-80	20	30	22	Dark brown
7	A6063T ₅	Sulfophthalic acid. 60g/l	Formic acid. 15g/l	Sulfuric acid 0.04g/l	3.0	45-75	20	12	9	Umbre
8	A6063T ₅	Sulfosalicylic acid. 60g/l	Formic acid. 60g/l	Sulfuric acid 0.04g/l	3.0	45-75	20	12	9	Olive (1)
10	A1100	Sulfophthalic acid. 70g/l	Ammonium formate. 20g/l	Sulfuric acid 1.0g/l	2.0	40-80	20	20	10	Umbre
11	A6063T ₅	Sulfosalicylic acid. 65g/l	Nickel formate. 40g/l	Sulfuric acid 1.2g/l	2.0	50-100	20	29	15	Light bronze

Note: (1) The surface was "satin finish".

WHAT WE CLAIM IS:—

1. A method of producing colored anodic coating on aluminum and its alloys comprising: providing at least one cathode;

5 immersing the aluminum or its alloys as an anode into an aqueous electrolyte comprising aromatic sulfonic acid;

10 passing a direct current through the electrolyte solution between the anode and cathode to obtain a colored anodic coating on the aluminum or its alloy;

15 wherein an improvement comprises employing, as said aqueous electrolyte, an aqueous electrolyte solution containing (a) aromatic sulfonic acid and (b) at least one member selected from formic acid and formate salts.

2. A method according to claim 1, wherein said aromatic sulfonic acid is contained in the electrolyte in an amount of 10 to 500 g/litre, and said at least one member is contained in the electrolyte in an amount of from 5 to 200 g, in terms of the weight of formic acid, per litre of the electrolyte, and, further, said direct current is passed at a current density of from 0.5 to 5 ampere/square decimeter of aluminum (alloy) surface over the period of 1 to 150 minutes and a voltage of from 20 to 120 volts is applied between the anode and the cathode.

3. A method according to claim 2, wherein said direct current is passed at a current density of 1 to 3 ampere/square decimeter of aluminum (alloy) surface over the period of from 5 to 20 minutes and a voltage of from 25 to 80 volts is applied, thereby obtaining a colored anodic coating having a thickness ranging from 2 to 20 microns.

4. A method of producing colored anodic coating on aluminum and its alloys comprising:

40 providing at least one cathode; immersing the aluminum or its alloys as an anode into an aqueous electrolyte comprising aromatic sulfonic acid;

45 passing a direct current through the electrolyte solution between the anode and cathode to obtain a coating of colored anodic coating on the aluminum or its alloy;

wherein an improvement comprises employ-

ing, as said aqueous electrolyte, an aqueous electrolyte solution of (a) aromatic sulfonic acid, (b) at least one member selected from formic acid and formate salts and (c) at least one member selected from sulfuric acid and water soluble sulfate or bisulfate salts.

5. A method according to claim 4, wherein said aromatic sulfonic acid (a) is contained in the electrolyte in an amount of from 10 to 500 g/litre and said at least one member (b) is contained in the electrolyte in an amount of from 5 to 200 g, in terms of the weight of formic acid, per litre of the electrolyte, and said at least one member (c) is contained in the electrolyte in an amount not higher than 5 g, in terms of the weight of the sulfuric acid, per litre of the electrolyte, and, further, said direct current is passed at a current density of from 0.5 to 5 ampere/square decimeter of aluminum (alloy) surface over a period of 1 to 150 minutes and a voltage of from 20 to 100 volts is applied between the anode and the cathode.

6. A method according to claim 5, wherein said at least one member (c) is contained in the electrolyte in an amount of from 0.5 to 2 g, in terms of the weight of the sulphuric acid per litre of the electrolyte.

7. A method according to any one of claims 1, 2, 4 and 5, wherein said aromatic sulfonic acid is sulfophthalic acid.

8. A method of producing colored anodic coating on aluminum and its alloys according to Claim 1 and substantially as hereinbefore described in any one of the specific embodiments.

9. An article of aluminum or of an aluminum alloy having a colored anodic coating produced by a method according to any preceding Claim.

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